

Preparation of Synthetic Stones for Denim Washing and Analysis of Wash Effects

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Abstract- Synthetic stones have been prepared with different chemical compositions selected statistically using Box and Behnken model. The linear regression analysis figures have been obtained using MATLAB to evaluate the extent of modification in recipes on the basis of hardness. The Mohs hardness scale has been used to evaluate the hardness of the stones. Various properties of the synthesized stones were evaluated.

The effects of synthetic and natural pumice stones on denim washing were compared. The washing was done in presence and absence of various fading agents and cellulase enzyme. A particular composition of stone was found to give the best result. Synthesized stone is found to be a better substitute to natural pumice stones.

Keywords- Denim; Pumice Stone; Synthetic Stone; Washing

I. INTRODUCTION

Denim is one of the world's oldest fabrics, and yet it remains eternally young. It was traditionally colored blue with indigo dyes to make blue jeans, although jeans denoted a different lighter cotton textile. Stonewashed jeans were a popular fashion trend in the 1980s. They have been treated to produce vintage look on the garments, because of varying degree of abrasion in the area such as waistband, pocket, seam and body. Traditionally, denim jeans manufactures wash their garments with natural pumice stones or enzymes [1-3]. A major drawback of natural pumice stones is their easy breakability during washing which creates environmental problems.

The present work was, therefore, aimed at replacing natural pumice stones with artificially synthesized stones which are having all the major properties of volcanic grade natural pumice stones and can overcome the problem occurring with natural stones during denim washing. Different statistical analysis were carried out in order to optimize and finding out the best recipe for synthetic stone preparation. A number of trials were taken with many recipes and finally a level, for each ingredient, was set and fed to the Box and Behnken model to have fifteen levels/recipes. The synthetic stone balls were prepared and their hardness was examined. The recipes were statistically evaluated on the basis of their hardness using MATLAB. After its preparation different properties of stones were checked like hardness in terms of Mohs, wetting time, weight loss due to treatments. Best recipe was chosen for washing effect analysis in presence and absence of different fading agents. The performance of synthesized stone was compared with natural stone with respect to various physical properties and washing effect on denim.

II. MATERIALS & METHODS

PART A: Synthesis of stones and evaluation of their properties:

The synthetic stones were prepared by combining filler material, bonding agent and abrasive material.

TABLE I OPTIMIZATION OF RECIPE BY BOX-BEHNKEN MODEL; VARIABLES AND THEIR LEVELS USED IN THE EXPERIMENT

Variable	Level		
	-1	0	+1
Al ₂ O ₃	30	40	50
SiO ₂	15	20	25
CaCO ₃	5	10	15

The stones were prepared using calcium carbonate as filler material, silicon dioxide and aluminium oxide as abrasive materials and cement & sand were used as bonding agents [4]. The recipes were selected so as to prepare synthetic stones to resolve the drawbacks of volcanic grade natural pumice stones with respect to hardness and absorbency. So, both these properties of each ball were checked. The recipes were designed statistically using Box-Behnken model with three independent variables and three levels of each variable as shown in Table I and Table II. All the balls were of equal weight. After preparing the balls various properties like hardness and wetting time were measured.

TABLE II RECIPES USED IN THE PREPARATION OF BALLS AND LEVELS OF THE INGREDIENTS USED

Composition Code (CC)	Level			% Composition		
	Al ₂ O ₃	SiO ₂	CaCO ₃	Al ₂ O ₃ (X ₁)	SiO ₂ (X ₂)	CaCO ₃ (X ₃)
1	-1	-1	0	30	15	10
2	1	-1	0	50	15	10
3	-1	1	0	30	25	10
4	0	-1	-1	40	15	05
5	1	0	1	50	20	15
6	-1	0	-1	30	20	05
7	1	0	-1	50	20	05
8	0	0	0	40	20	10
9	-1	0	1	30	20	15
10	1	1	0	50	25	10
11	0	0	-1	40	25	05
12	0	-1	1	40	15	25
13	0	1	1	40	25	15
14	0	0	0	40	20	10
15	0	0	0	40	20	05

Note: In all the recipes cement & sand were used in the ratio 5:2

Regression analysis on the basis of hardness of the stones with respect to concentration of any two ingredients (Al₂O₃, CaCO₃ or SiO₂) was studied using MATLAB. The prepared balls were then dried in an oven at temperature 100°C

Determination of various properties of synthesized balls:

- Determination of hardness:

It was measured on machine Monsanto Tensometer-20 which has given the hardness of prepared synthetic balls in N/mm^2 which was converted into Mohs unit using Eq. (1).

$$\text{Log}(H \times 9.8) = 0.2 M + 1.5 \quad (1)$$

Where, M = Mohs number and H = hardness in N/mm^2 .

- Statistical analysis:

In statistics, regression analysis included the technique for modelling and analysing several variables, when the focus was on the relationship between a dependent variable (hardness H) and one or more independent variables (ingredients used). The relation of linear regression through MATLAB was studied for examining the change in the hardness of the synthesized balls with respect to concentration of any two ingredients from Al_2O_3 , $CaCO_3$ and SiO_2 in the recipe.

- Determination of wetting time :

The wetting time, in seconds, of synthesized stones was determined by drop penetration test.

- Determination of weight loss (%):

The synthetic stones were checked for surface etching in acids, alkalies and neutral conditions. The treatment was done under controlled conditions in lauderometer. The weight loss (%) of the treated stones was calculated from the weight difference before and after the washing treatment.

PART B: Washing of denim using synthetic stones and its comparison with natural pumice stone

1) Denim desizing:

The desizing of denim was carried out by enzymatic desizing. The desizing was done using amylase enzyme under the treatment conditions as shown in Table III.

TABLE III DESIZING CONDITION

Sr. No.	Parameters	
1	Temperature	55°C
2	pH	5.5
3	Liquor Ratio	1:30
4	Process Time	45 min

2) Denim washing:

Washing of the desized denim samples for colour fading was conducted using natural pumice stone as well as prepared synthetic stones in presence and absence of different fading agents.

- Washing of denim with natural pumice stones in absence of any fading agent:

The washing of the denim samples were done in lauderometer for 45 minutes. For this treatment certain specific small sized volcanic grade pumice stones were taken for the test. Samples were taken out dried and tested further.

- Washing of denim with synthesised stones in absence of any fading agent

The denim samples were washed with different synthesised stones made using varying combinations as discussed earlier. The results were compared with wash effects using natural pumice stone used in identical condition.

- Washing of denim with stones in presence of enzyme:

The denim fabric samples were washed with stones along with cellulase enzyme as per the process parameters shown in Table IV.

TABLE IV WASHING PARAMETERS-1 (STONES+ENZYMES)

Sr. No.	Parameters	
1	Temperature (°C)	50
2	pH	5.5
3	Liquor ratio	1:30
4	Process time (minutes)	45

- Washing of denim with stones in presence of sodium hypochlorite:

The denim fabric samples were washed with stones along with sodium hypochlorite as per the process parameters shown in Table V.

TABLE V WASHING PARAMETERS-2 (STONES + SODIUM HYPOCHLORITE)

Sr. No.	Parameters	
1	Temperature (°C)	50
2	pH	10
3	Liquor ratio	1:30
4	Process time (Minutes)	45

- Washing of denim with stones in presence of peracetic acid :

In-house peracetic acid was prepared as per the method suggested elsewhere [5] and the fabric samples were treated as per the method given in Table VI.

TABLE VI WASHING PARAMETERS-3 (STONES + PERACETIC ACID)

Sr. No.	Parameters	
1	Temperature	60°C
2	pH	5.5
3	Liquor ratio	1:30
4	Process time	45 min

The washing of the fabric samples in PAA was carried out in presence of sodium hexameta phosphate and trisodium phosphate as buffering agent for maintaining the pH.

3) Process sequence in washing:

Following sequence was followed in washing:-

- Stones were added (synthetic/natural) into the treatment bath.

Desized denim fabric was then entered into the machine (1.5 part weight stones per weight of the fabric sample).

- Required chemicals were added (enzyme/PAA/NaOCl).
- Tumbling was done under standard conditions in lauderometer.

- The solution was drained.

- Denim samples were taken out

The samples were rinsed and dried. The treated samples were then tested for various characterization techniques.

4) Characterization of washed denim:

The washed denim was characterized as discussed in the following section

- Determination of colour strength:

The colour strength was measured in terms of K/S using Premier Colour Scan 5100 Spectrophotometer interphase with computer colour matching System. The colour strength of the samples was compared with the corresponding values of the control sample i.e. desized sample.

- Determination of tensile strength:

For testing the load and elongation at break values, fabric of length 20 cm and width 5 cm was mounted on a Lloyds tensile-tester at a cross-head speed of 300 mm/min, with a gauge length of 200 mm.

- Scanning Electron Microscopic study (SEM):

SEM microphotographs of denim fabric were recorded at magnification of 25x using a SEM-Model JSM 5610LV, version 1.0, Jeol, Japan. The standard procedure was followed in order to measure the SEM photographs of the denim samples. The SEM photographs of all the washed samples were compared with the control sample to analyze the effect of washing.

III. RESULTS & DISCUSSIONS

The denim samples were washed using natural as well as prepared synthetic stones in presence and absence of different fading agents viz cellulase enzyme, sodium hypochlorite and peracetic acid. The effects of such treatments on the properties of the denim samples were investigated and presented here.

Part A: Synthesis of stone and evaluation of properties

The stones were produced from 15 different recipes generated from the Box & Behnken model (Table VII). These synthetic stone balls were subjected to evaluation of hardness and the results are shown in Table VIII. In order to increase the strength of the balls, Ferric Oxide Fe_2O_3 was initially added to all the recipes in a very small proportion (0.2 %), but it was found that the addition of ferric oxide generated drawbacks like pink turbidity of treatment solution. Addition of Fe_2O_3 increased the strength drastically near about 8 Mohs but caused staining of the garments and therefore avoided in final selection.

TABLE VII RECIPES OBTAINED TO SYNTHESIZE SYNTHETIC STONES BALLS USING BOX-BEHNKEHN MODEL

Composition code (CC)	Recipe (%)		
	Al_2O_3	SiO_2	CaCO_3
1	31	15	10
2	50	15	10
3	30	25	10
4	40	15	05
5	50	20	15
6	30	20	05
7	50	20	05
8	40	20	10
9	30	20	10
10	50	25	10
11	40	25	05
12	40	15	15
13	40	25	15
14	40	20	10
15	40	20	05

TABLE VIII SHORT LISTED RECIPES FROM MATLAB

Composition code (CC)	Recipe (%)		
	Al_2O_3	SiO_2	CaCO_3
2	50	15	10
4	40	15	05
5	50	20	15
6	30	20	05
11	40	25	05
15	40	20	05

Effect of composition ingredients

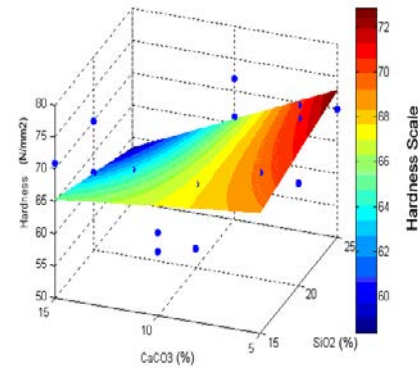


Fig. 1 Regression analysis of hardness against concentration of calcium carbonate and silicon dioxide

It can be clearly seen from the Fig. 1 that the hardness of the balls increased with increase in the amount of SiO_2 and reduction in the amount of CaCO_3 .

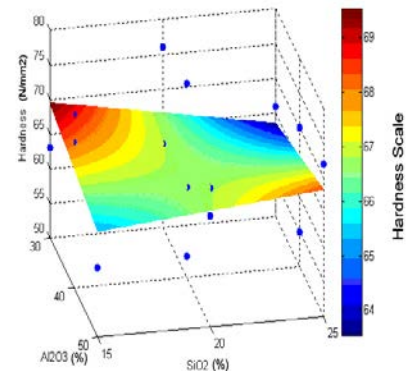


Fig. 2 Regression analysis of hardness against concentration of aluminium oxide and silicon dioxide

It is evident from Fig. 2 that the hardness of the synthesized stones increased with increasing the amount of aluminium oxide against silicon dioxide 30% Al_2O_3 and 15% SiO_2 produced best results.

Fig. 3 shows that lowering the concentration of CaCO_3 was found to have a positive effect on improving the hardness of the stones when compared with the concentration of alumina which also support the results presented in Fig. 1.

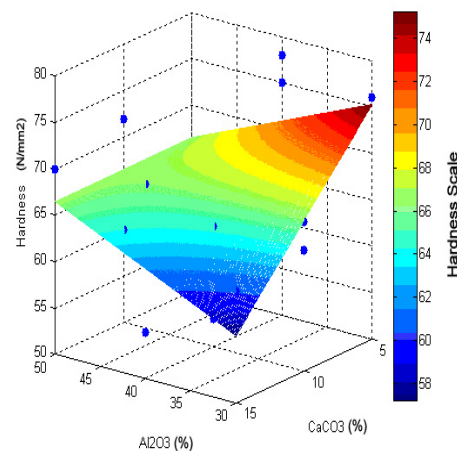


Fig. 3 Regression analysis of hardness against concentration of calcium carbonate and aluminium oxide

Linear regression analysis helped us in obtaining 6 acceptable recipes (Table VIII) having reasonably good

hardness of the synthetic stones. Composition code 15 produced a hardness of 78 N/mm² which corresponds to approximately 7 in Mohs scale (Table IX).

TABLE IX THE BREAKING STRENGTH OR HARDNESS OF SYNTHESIZED STONES

Composition code (CC)	Hardness (N/mm ²)	Hardness (Mohs scale)
1	63	6
2	60	6
3	66	6
4	75	7
5	70	7
6	76	7
7	66	6
8	63	6
9	62	6
10	72	7
11	70	7
12	71	7
13	55	6
14	53	6
15	78	7

1) Analysis of wetting time/absorbency of balls:

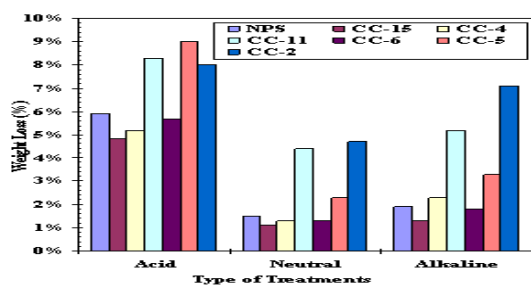
The wetting time of all the synthetic stone balls are given in Table X. It is evident from this table that the selected six compositions were having good absorbency. Stones prepared using these six recipes (Table VIII) were therefore chosen for further study. The stone prepared using composition code 13 took maximum time to wet.

TABLE X WETTING TIME OF STONES

Stone type		Wetting time (sec)
Natural pumice stone		1.8
SYNTHETIC STONE	CC-1	6.4
	CC-2	2.0
	CC-3	4.9
	CC-4	1.1
	CC-5	1.8
	CC-6	1.4
	CC-7	7.2
	CC-8	5.2
	CC-9	6.1
	CC-10	4.6
	CC-11	1.6
	CC-12	3.1
	CC-13	9.4
	CC-14	4.3
	CC-15	0.9

2) Effect of treatment condition on the weight loss of stone balls:

As the stone washing process may be acidic, alkaline or neutral selected synthesized balls having composition code 15, 4, 5, 6, 11 and 2 were subjected to acidic, alkaline and neutral tumbling to examine the loss in weight due to such treatments. The results are shown in Fig. 4.



Note: NPS denotes natural pumice stone

Fig. 4 Weight loss of stones due to tumbling under different fading conditions

It is found that the natural stone showed very high loss in weight when subjected to different fading agents and stones prepared using composition code 15, 4, 6, and 2 were having good resistance against surface etching compared to natural pumice stones (NPS). From all these results balls synthesized using composition code 15 was selected for denim washing studies reported in the following section.

Part B: Washing of denim using synthetic stones and its effects

1) Effect of stone washing on colour fading of denim:

Fig 5 compared the losses in colour under different fading agents in case of washing of denim samples using natural pumice stone and stones prepared using composition code 15. It is clearly seen from the results given in Table XI & Table XII that the colour fading of denim were higher for synthetic stones compared with the natural stones and NaOCl caused maximum fading in colour in both the cases.

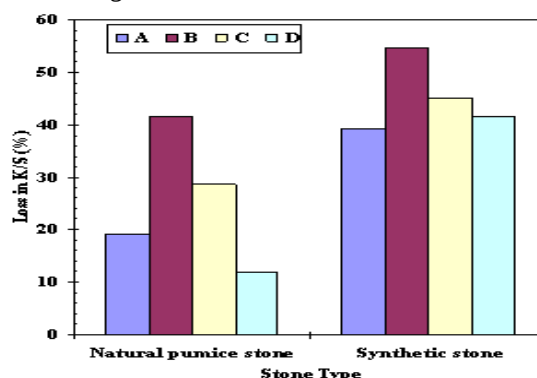


Fig. 5 Effect of denim washing under varying fading agents using natural pumice stones and synthetic stones of composition code 15 (A- only stone wash, B- stone wash in presence of NaOCl, C- stone wash in presence of enzyme, D- stone wash in presence of CH₃COOH)

TABLE XI EFFECT OF DENIM WASHING UNDER VARYING FADING AGENTS USING NATURAL PUMICE STONES

Sr. No.	Sample	K/S
1	Desized denim (Control sample)	8.4
2	Only stone wash	6.8 (19.0)
3	Stone wash in presence of NaOCl	4.9 (41.6)
4	Stone wash in presence of enzyme	6.0 (28.5)
5	Stone wash in presence of peracetic acid	7.4 (11.9)

Values in parenthesis indicate % loss in K/S

TABLE XII EFFECT OF DENIM WASHING UNDER VARYING FADING AGENTS USING SYNTHETIC STONES OF COMPOSITION CODE 15

Sr. No.	Sample	K/S
1	Desized denim (Control sample)	8.4
2	Only Stone wash	5.1 (39.2)
3	Stone wash in presence of NaOCl	3.8 (54.7)
4	Stone wash in presence of enzyme	4.6 (45.2)
5	Stone wash in presence of peracetic acid	4.9 (41.6)

Values in parenthesis indicate % loss in K/S

2) Effect of stone washing on tensile properties of the denim:

The stone washing caused a reduction in strength whereas elongation at break was increased corresponding to the control sample.

TABLE XIII EFFECT OF STONE WASHING ON TENSILE PROPERTIES OF DENIM

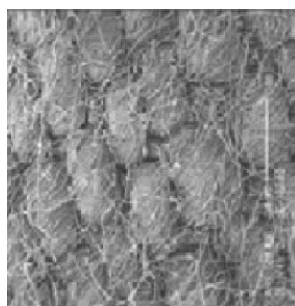
Sr. No.	Samples	Strength (N/mm ²)		Elongation (%)	
		Warp	Weft	Warp	Weft
1	Desized denim (Control sample)	71.6	47.3	28.1	18.9
2	Only stone washed (Natural pumice stone)	59.3 (17.1)	44.1 (6.7)	31.5 (12.0)	21.1 (11.6)
3	Only stone washed (synthetic stone CC-15)	56.7 (20.8)	42.4 (10.3)	34.1 (21.3)	20.3 (7.4)
4	Synthetic stone wash (CC-15) in presence of sodium hypochlorite	47.5 (33.6)	37.3 (21.1)	36.1 (28.4)	19.7 (4.2)
5	Synthetic stone wash (CC-15) in presence of enzyme	53.7 (25.0)	41.0 (13.3)	38.2 (35.9)	21.6 (14.2)
6	Synthetic stone wash (CC-15) in presence of peracetic acid	51.9 (27.5)	43.6 (7.8)	32.7 (16.3)	20.9 (10.5)

Values in parenthesis indicate % loss in tensile strength and % gain in elongation

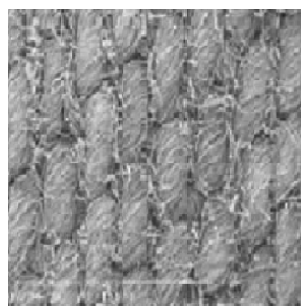
The washing of denim both with natural as well as synthetic stones caused some reduction in strength accompanied by increased elongation. The presence of fading agents further increased the extent of loss in strength. Sodium hypochlorite as a fading agent caused maximum loss in strength followed by peracetic acid and cellulase enzyme. The results of strength losses are in accordance with the losses in weight (Fig. 4).

3) Analysis of scanning electron microphotography of different denim washed samples:

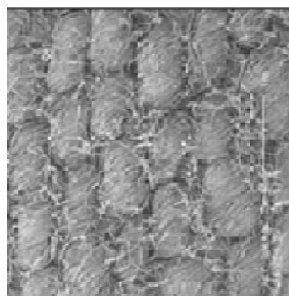
SEM microphotographs presented in Fig. 6 shows that the surface hairs are reduced due to the abrasion of stones on the denim samples (Fig. 6b & 6c). But both NaOCl and Peracetic acid raised surface hairs. Careful examination of the microphotographs reveals that synthetic stones when used alone faded the colour more compared with the one treated with only natural stone which is also supported by the colour values given in Table XI & XII



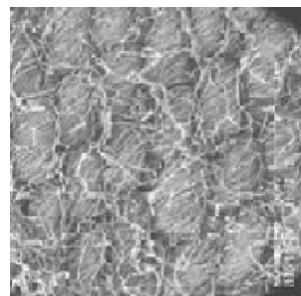
a



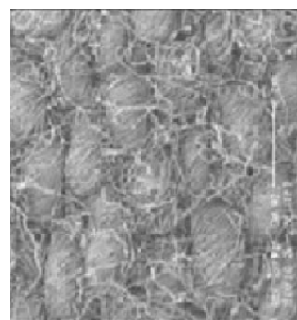
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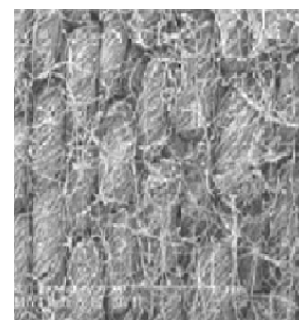
c



d



e



f

Fig. 6 Scanning Electron Microphotographs of denim samples (25×)
a- desized denim (control sample); b- only stone washed (natural pumice stone);
c- only stone washed (synthetic stone); d- washed with synthetic stone + NaOCl; e- washed with synthetic stone + Cellulase; f- washed with synthetic stone + peracetic acid)

IV. CONCLUSIONS

The present work was aimed at replacing natural pumice stones with artificially synthesized stones for washing of denim. Synthetic stones were prepared by combining filler material, bonding agent and abrasive material. The bonding agents served in holding the filler particles together during the formation of the stones, e.g. cement/sand. The abrasive material like SiO₂/Al₂O₃ used to have abrasive property of the stone required during subsequent use. Filler material used was CaCO₃.

The synthetic stone balls were prepared and their hardness was examined. Among all the ingredients aluminium oxide was found to play major role in obtaining good hardness in stones. The recipes were statistically evaluated on the basis of their hardness using MATLAB. Six recipes were selected for the studies on weight loss during washing treatments and wetting time of the stones. From the results of the later, composition code 15 was found to be the best. The stone prepared using composition code 15 gave much better results in respect of strength, wetting time and fading compared with the natural pumice stone. Therefore natural stones used for denim washing may be well replaced by the synthetic stones which would result better effect with less grit formations.

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